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TI **Copper** alloy **foil** having high strength, conductivity and heat resistance
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AB The **Cu** alloy **foils** contain Cr 0.02-0.4, Zr 0.01-0.25, Zn 0.02-2.0, and optionally Ni, In, Mn, P, Mg, Al, B, As, Cd, Co, Te, Ag and/or Hf 0.005-1.5 wt.%, and the size and no. of inclusions are .ltoreq.10 .mu.m and <100/mm2, resp. The **Cu** alloy **foils** are used for flexible printed boards or integrated circuit tape carriers, etc.

PATENT ABSTRACTS OF JAPAN

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(30)Priority

Priority number : 09 91337 Priority date : 27.03.1997 Priority country : JP

(54) COPPER ALLOY FOIL

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a Cu-Cr-Zr type copper alloy foil excellent in productivity as well as in strength, electric conductivity, and heat resistance.

SOLUTION: This copper alloy foil has a composition consisting of by weight, 0.02-0.4% Cr, 0.01-0.25% Zr, 0.02-2.0% Zn, and the balance copper with inevitable impurities and containing, if necessary, 0.05-1.8% Fe and 0.05-0.8% Ti and further containing, if necessary, 0.005-1.5 wt.% in total, of one or more elements among Ni, Sn, In, Mn, P, Mg, Al, B, As, Cd, Co, Te, Ag, and Hf. Moreover, the size of inclusions in this copper alloy foil is regulated to ≤10 μm, and also the number of inclusions having a size of 0.5 to 10 μm is regulated to <100 pieces/mm2.

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* NOTICES *

CLAIMS

[Claim(s)]
[Claim 1] The number of the inclusion of the size which Cr:0.02-0.4%, Zr:0.01-0.25%, and Zn:0.02-2.0% are contained at a weight rate, and the remainder consists of copper and an unescapable impurity, and the size of inclusion is 10 micrometers or less, and is 0.5-10 micrometers is 2 100 pieces/mm. Copper alloy foil characterized by being the following.
[Claim 2] The copper alloy foil characterized by the following. At a weight rate, they are Cr:0.02-0.4%, Zr:0.01-0.25%, and Zn:0.02-2.0%. Furthermore, one or more sorts of nickel, Sn, In, Mn, P, Mg, aluminum, B, As, Cd, Co, Te, Ag, and Hf: The number of the inclusion of the size which no less than 0.005 - 1.5 % of the weight is contained in a total amount, and the remainder consists of copper and an unescapable impurity, and the size of inclusion is 10 micrometers or less, and is 0.5-10 micrometers is 2 100 pieces/mm. Following.
[Claim 3] The number of the inclusion of the size which Cr:0.02-0.4%, Zr:0.01-0.25%, and Zn:0.02-2.0% are contained at a weight rate, Fe:0.05-1.8% and Ti:0.05-0.8% are also contained further, the remainder consists of copper and an unescapable impurity, and the size of inclusion is 10 micrometers or less, and is 0.5-10 micrometers is 2 100 pieces/mm. Copper alloy foil characterized by being the following.
[Claim 4] At a weight rate, Cr:0.02-0.4%, Zr:0.01-0.25%, Zn:0.02-2.0% is contained. further Fe:0.05-1.8%, Ti:0.05-0.8% is contained and added. nickel, Sn, In, Mn, One or more sorts of P, Mg, aluminum, B, As, Cd, Co, Te, Ag, and Hf : No less than 0.005 - 1.5 % of the weight is contained in a total amount. The number of the inclusion of the size which the remainder consists of copper and an unescapable impurity, and the size of inclusion is 10 micrometers or less, and is 0.5-10 micrometers is 2 100 pieces/mm. Copper alloy foil characterized by being the following.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[The technical field to which invention belongs] this invention relates to the copper alloy foil excellent in intensity, thermal resistance, and productivity. This copper alloy foil is suitable for uses, such as a flexible printed circuit board and IC tape career.
[0002]
[Description of the Prior Art] It is the feature to have flexibility, and since a flexible printed wiring board can be bent, or twisted and contained in electronic equipment, on the occasion of the miniaturization of electronic equipment, a space can be effectively used for it, and also it is used for wiring to moving part. Moreover, in the field of the integrated circuit, the package using the tape career of the copper foil which can respond to ** pitch-ization is conventionally used with the formation of ultra-thin little of a package. A flexible printed wiring board and IC tape career laminate copper foil to resins, such as a polyimide, and it unifies by adhesives or heating pressurization and they are formed. The above-mentioned circuit board can form the circuit pattern by which fine ** of the pitch was carried out by etching at about 50-100 micrometers.
[0003] Copper is the metal excellent in conductivity and it is common that the pure copper of about 99.99% of purity is used in the above-mentioned field by which high conductivity is thought as important. However, since intensity and a heat-resistant fall would become remarkable if purity is raised, the problem of deformation and an open circuit occurred by heating at the time of laminating in flexible resin substrates, such as a polyimide, and copper had the defect in which reliability fell. Moreover, when used in a place like the engine room of an automobile other than the heat history at the time of the above manufactures, in order to set under the environment around 100 degrees C, thermal resistance and heat shock-proof nature are needed.
[0004] On the other hand, if even the lamination foil of the above [the thickness of a foil] becomes thin in a manufacturing process, it will become difficult to roll out with the sufficient yield. Since especially the internal defect of inclusion etc. becomes the cause which fracture and a pinhole produce at the time of rolling, it reduces productivity, as a result causes increase of a manufacturing cost. Therefore, a material is expected for there to be little inclusion.
[0005] By the way, a deposited type copper alloy is used on the use of which the high intensity and high conductivity like the copper alloy for electronic equipment are required in many cases in recent years. A Cu-Cr-Zr system alloy is a typical deposited type copper alloy having high intensity and high conductivity, and the utilization as a charge of electronic equipment material is tried. According to the research result in this alloy, when detailed Cr and a detailed Cu3 Zr deposit particle arise in a copper matrix in aging deposit process, it is supposed that intensity and conductivity will rise and it is supposed that it is the size of the deposit particle which contributes to an on-the-strength rise 0.5 micrometers or less.
[0006] For example, the patent official report of a patent number No. (registration day : March 13, Heisei 8) 2501275 chooses zirconium 0.005 - 1wt% either or both sides chromium 0.01 - 2wt%, and becomes 60 ppm or less of oxygen, and a remainder real target from copper, and the size of a sludge is 50 micrometers or less. And a 0.5-50-micrometer sludge is 2 100-100000 pieces/mm. The copper alloy which had the conductivity and intensity which are characterized by existing is indicated. It has also indicated adding nickel, Sn, Fe, Co and Zn of the amount of specification, and the alloying element of Ti and other a large number into this alloy. however, the size which amounts to no less than 50 micrometers -- a **** thing sludge -- 100-100000 piece/mm2.

existing -- if -- it is inapplicable as a rolling foil
[0007]
[Problem(s) to be Solved by the Invention] Although it is realizable since the property in which intensity and conductivity rise when detailed Cr and a detailed Cu3 Zr deposit particle arise in a copper matrix in a Cu-Cr-Zr system alloy has the property in which Cr and Zr of an alloying element cannot dissolve easily with the copper of a matrix The big and rough crystallization object or big and rough sludge which does not contribute to improvement in one side and intensity tends to remain in a matrix. moreover, since the activity of these alloying elements is high Since it is easy to generate an oxide, a sulfide, a silicide, etc., the result of being easy to become the organization which these comparatively big particles distributed in the matrix is to be induced. In fact, for the above-mentioned patent number No. 2501275, a 0.5-50-micrometer sludge is 2 100-100000 pieces/mm. It reached and has indicated existing.
[0008] A Cu-Cr-Zr system alloy is an outstanding copper alloy which has high intensity and high conductivity fundamentally, and using this also for rolling copper foil is expected. However, if these big and rough particles exist, since it will become the cause which fracture and a pinhole produce at the time of rolling in putting a Cu-Cr-Zr system alloy in practical use as a copper alloy foil material, productivity is reduced, as a result increase of a manufacturing cost is caused.
[0009] Therefore, while having the intensity, the outstanding conductivity, and outstanding thermal resistance which can be used suitable for a flexible printed circuit board or IC tape careers, development of the Cu-Cr-Zr system copper alloy foil excellent also in productivity is demanded. Moreover, in such a copper alloy foil, it is also required to prevent the soldered joint section producing ablation with working heat in the use in a flexible printed circuit board etc.
[0010]
[Means for Solving the Problem] As a result of repeating research of a Cu-Cr-Zr system alloy, while this invention persons adjust an alloy content by adding Zn to Cr and Zr By controlling and selecting manufacture conditions strictly and controlling a distribution of inclusion, such as a sludge in a matrix, a crystallization object, an oxide, a sulfide, and a silicide It is possible to make intensity, conductivity, thermal resistance, and productivity balance on high level. The bird clapper turned out that the further improvement of a strength property was possible by adding one or more sorts of Fe, Ti, and nickel, Sn, In, Mn, P, Mg, aluminum, B, As, Cd, Co, Te, Ag and Hf to this. Unlike the indication of the aforementioned patent number No. 2501275, the number of the inclusion of the size which the size of inclusion is 10 micrometers or less, and is 0.5-10 micrometers is 2 100 pieces/mm. It could consider as the following and the copper alloy rolling foil which can begin by this and can be used suitable for a flexible printed circuit board, IC tape career, etc. was obtained.
[0011] It is based on such knowledge. this invention Cr:0.02-0.4%, Zr:0.01-0.25%, Zn:0.02-2.0% is contained. as occasion demands Fe:0.05-1.8%, Ti:0.05-0.8% -- further -- the need -- nickel, Sn, In, and Mn -- One or more sorts of P, Mg, aluminum, B, As, Cd, Co, Te, Ag, and Hf : No less than 0.005 - 1.5 % of the weight is contained in a total amount. The remainder consists of copper and an unescapable impurity, and the size of inclusion is 10 micrometers or less. and the number of inclusion with a size of 0.5-10 micrometers -- 100 piece/mm2 It is characterized by being the following, and intensity and thermal resistance are markedly boiled rather than conventional copper foil, it improves, and a copper alloy foil also with still better productivity is offered.
[0012] In this invention with a term "inclusion" The cooling process after the solidification process at the time of casting (i.e., the solidification back), The sludge produced at a deposit reaction in the matrix of solid phase at the time of the cooling process after hot rolling, and aging annealing etc. (particle), The oxide which is an impurity which produces according to the segregation of the solidification process at the time of casting, and is generally produced by the reaction within a big and rough crystallization object (particle) and the molten metal at the time of the dissolution, a sulfide, a silicide, etc. are used as what includes the particle observed by microscope observation of this copper alloy in a matrix. "The size of inclusion" says the minimum diameter of circle which wraps the inclusion for inclusion in the bottom of microscope observation. "The number of inclusion" is the average number of the inclusion per [which were actually counted in the part under microscope observation] unit square mm. That is, after carrying out mirror polishing of the front face of a sample, in EPMA, it is 5000 times the scale factor of this, and the number of inclusion with a size [per unit square mm] of 0.5-50 micrometers is measured.

[0013]
[Embodiments of the Invention] The reason which limited alloy composition and the inclusion size as mentioned above in this invention is explained.
(Cr) Although Cr carries out the operation which deposits in a host phase and raises intensity by carrying out aging of the alloy after solution treatment, at less than 0.02 % of the weight, the effect of a request according [the content] to this operation is not acquired, but if it is made to contain exceeding 0.4%, on the other hand, big and rough Cr will remain in a host phase. Consequently, the fall of productivity will be caused by the fracture at the time of rolling, pinhole generating, etc. By such reason, Cr content determined it as 0.02 - 0.4% of the weight of the range.
[0014] (Zr) Although Zr had the operation which forms Cu and a compound by the aging treatment, deposits in a host phase, and strengthens this, the effect of a request according [the content] to the aforementioned operation was not acquired, but since big and rough un-dissolving [Zr] came to contain and the fall of productivity caused after solution treatment when Zr was made to contain exceeding 0.25 % of the weight, on the other hand at less than 0.01 % of the weight, a Zr content determined it as 0.01 - 0.25 %.
[0015] (Zn) Although Zn was a component added in order for the soldered joint section to prevent producing exfoliation with working heat, at less than 0.02%, the effect of a request according [the content] to the aforementioned operation was not acquired, but when Zn was made to contain exceeding 2.0, on the other hand, the decline in conductivity determined Zn content as 0.02 - 2.0% from the bird clapper remarkably.
[0016] (Ti and Fe) Although Ti and Fe are added if needed in order to demonstrate the operation which forms the intermetallic compound of Ti and Fe into a host phase, and raises alloy intensity further as the result when the aging treatment of the alloy is carried out, at less than 0.05%, the intensity of a request according [these contents] to the above-mentioned operation is not obtained, respectively. On the other hand, when Ti content exceeds 0.8% or Fe content exceeds 1.8%, the big and rough inclusion which makes Ti and Fe a principal component comes to be contained, and productivity is checked remarkably.
[0017] (nickel, Sn, In, Mn, P, Mg, aluminum, B, As, Cd, Co, Te, Ag, Hf) Although each of these has the operation which raises intensity mainly by solid solution strengthening, without reducing the conductivity of an alloy, therefore one sort or two sorts or more of addition is made as occasion demands The effect of a request according that the content is less than 0.005% in a total amount to the aforementioned operation is not acquired, but when exceeding 1.5% in a total amount by one side, conductivity is degraded remarkably, and productivity also falls. For this reason, the content of nickel, Sn, In, Mn, P, Mg, aluminum, B, As, Cd, Co, Te, Ag, and Hf by which independent addition or two or more sorts of compound addition are made determined it as 0.005 - 1.5% in the total amount.
[0018] (Inclusion) By this alloy system, the particle of inclusion may exist in a matrix. Although the inclusion for obtaining intensity required for this alloy is small, the big and rough inclusion exceeding 0.5 micrometers is set like about [not contributing to on-the-strength elevation] and a roll turner, generates fracture and a pinhole, and causes a productivity fall. In order not to cause such fault, the upper limit of the size of this big and rough inclusion is set to 10 micrometers, and they are 2 / mm2 100 pieces/mm about the number of inclusion with a size of 0.5-10 micrometers. What is necessary is just to consider as the following.
[0019] Next, the manufacture method for obtaining this alloy is explained.
(The dissolution and casting) It is important to prevent generation of inclusion, such as a big and rough oxide, a sulfide, and a silicide, at a dissolution process. First, as the quality of the material of a crucible, carbon is desirable, and the use is not appropriate, in order for a molten metal to eat these away, and to involve in into a molten metal, or for internal insulation to be returned by Zr and to generate Zr oxide, when using the thing containing oxides, such as a magnesia, an alumina, and a silica. Moreover, if the dissolution raw material to be used has adhesion of an oil content, since a sulfide may be formed in a molten metal, it is not desirable. Therefore, when using return material, it should degrease or use of return material should be avoided. After the melt down of a dissolution raw material needs to reduce an oxygen density by covering a molten-metal front face with reducing gas, such as CO, or considering as vacuum atmosphere. It is desirable to set an oxygen density to 20 ppm or less by this.
[0020] (Homogenization heat treatment) Next, homogenization heat treatment conditions are described. In an ingot, the crystallization object formed when alloying elements including Cr and Zr segregated at the time of

casting exists. In order to make these small in the process to a product, it is necessary to make a crystallization object small in this stage by carrying out enough, before hot-rolling homogenization heat treatment. It is necessary to specifically make preferably 800 degrees C or more of temperature in a hot rolling start time into 850 degrees C or more.

[0021] (Hot rolling) Next, hot rolling conditions are described. If temperature falls during rolling, when a deposit reaction progresses, big and rough-ization of a particle will take place. In such a case, a large particle will remain also in a product stage. Therefore, it is required during hot rolling for the temperature of material not to fall, and it is desirable for 700 degrees C or more to be 750 degrees C or more preferably about end temperature. In the cooling process after hot rolling, when a deposit reaction progresses, big and rough-ization of a particle takes place, so that a cooling rate is made late. In such a case, a large particle will remain also in a product stage. Therefore, it is required during hot rolling for the temperature of material not to fall, and it is desirable for 700 degrees C or more to be 750 degrees C or more preferably about end temperature.

[0022] (Solution treatment) Liquid-ized processing is performed for obtaining the material of high intensity by the next aging treatment. The intensity after the increase of the amount of dissolution into the matrix of Cr and Zr and aging becomes [the one where processing temperature is higher] high. It is so good that processing temperature is high in order to acquire such an effect, and it is desirable to consider as 700 degrees C or more. Moreover, as for a cooling rate, it is desirable in the case of solution treatment for high intensity to be easy to be obtained and for the quicker one to specifically perform water cooling.

[0023] (Cold rolling) If it cold-rolls after solution treatment, a deposit at an aging process will be promoted and high intensity will be obtained. Moreover, in order to acquire this effect, it is desirable to make workability of cold rolling into 40% or more.

[0024] (Aging treatment) The aging treatment is required in order to raise intensity and conductivity, and it is performed at 300-700 degrees C. The reason for making aging-treatment temperature into 300-700 degrees C requires time for an aging treatment at less than 300 degrees C, and is for Cr and Zr to dissolve, if it is not economical and exceeds 700 degrees C, and for the intensity and the conductive improvement by the age-hardening not to arise. Then, the last cold rolling and stress relief tempering are performed.

[0025]

[Example] this invention is explained based on an example and the example of comparison. First, electrolytic copper or an oxygen free copper is used as the main raw material, and it is a copper chromium hardener. A copper zirconium hardener, zinc, titanium, nickel, tin, an indium, manganese, magnesium mild steel, silicon, a copper Lynn hardener, aluminum, boron, an arsenic, cadmium, cobalt, a tellurium, and silver were made into the auxiliary material, and the copper alloy of the various component composition shown in Table 1 with a RF fusion furnace was [inside of vacuum, or Ar atmosphere] under dissolution using the crucible made from carbon, and it ingoted, and cast to the ingot with a thickness of 30mm. Next, according to the process mentioned above, the foil with a thickness of 0.035mm was created from each of these ingots, and it evaluated about "intensity", "conductivity", and "thermal resistance." About "intensity", tensile strength was measured in the tension tester. Conductivity showed "conductivity." "Thermal resistance" asked for the temperature which tensile strength reduces by half from before heating in heating for 1 hour as a softening temperature. In addition, about "the number of inclusion", after carrying out mirror polishing of the front face of a sample, in EPMA, it is 5000 times the scale factor of this, and the number of inclusion with a size [per unit square mm] of 0.5-50 micrometers was measured.

[0026] Moreover, thickness:0.035mm, width-of-face:450mm, length: The 5000m foil was created and evaluation of "productivity" was also performed. The inner fracture generating situation and the pinhole generating situation in a product stage estimated "productivity" like the roll turner. About "fracture", the case where fracture did not occur was made as O, and the case where it generated was made into x. About the "pinhole", it carried out by measuring the generating number of a pinhole with a diameter [per 1000m] of 0.5mm or more.

[0027]

[Table 1]

[0028]
[Table 2]

Table 1

表1　本発明合金および比較例

	No.	化学成分 (wt%)																				介在物数 (個/mm²)
		Cr	Zr	Zn	Tl	Fe	Sn	Ni	Si	Mg	P	In	Mn	Al	B	As	Cd	Co	Te	Ag	O (ppm)	Cu及び不純物	
本実施例	1	0.18	0.15	0.19	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	6	残	61
	2	0.26	0.08	0.28	−	−	0.07	−	−	−	−	−	−	−	−	−	−	−	−	−	10	残	65
	3	0.24	0.14	0.42	−	−	−	0.04	−	−	0.03	−	−	−	−	−	−	0.04	−	−	9	残	68
	4	0.22	0.18	0.26	−	−	−	−	0.15	−	−	−	0.09	−	−	−	−	−	−	−	13	残	88
	5	0.27	0.09	0.60	−	−	−	−	−	0.28	−	−	−	−	−	0.02	−	−	−	0.02	12	残	76
	6	0.34	0.12	0.19	−	−	−	−	−	−	−	0.06	−	−	−	−	−	−	0.04	−	8	残	78
	7	0.36	0.16	0.29	−	−	−	−	−	−	−	−	−	0.04	−	−	0.07	−	−	−	14	残	84
	8	0.20	0.18	0.72	0.22	0.29	−	−	−	−	−	−	−	−	−	−	−	−	−	−	13	残	88
	9	0.22	0.09	0.38	0.23	0.44	−	−	0.26	−	0.02	−	−	−	−	−	−	−	−	−	10	残	79
	10	0.23	0.14	0.89	0.37	0.61	0.11	−	−	0.18	−	−	0.07	−	0.09	−	−	−	−	−	8	残	85
比較例	11	0.03	−	0.21	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	7	残	80
	12	0.67	0.11	0.31	−	−	−	−	0.09	−	−	−	−	−	−	−	−	−	−	−	14	残	120
	13	0.26	0.14	2.12	0.31	0.62	−	1.02	0.21	−	−	−	−	−	−	0.02	−	−	−	−	8	残	89
	14	0.31	0.08	0.25	0.22	0.41	1.10	0.69	−	−	0.03	−	−	−	−	−	−	−	−	−	9	残	133
	15	0.29	0.22	0.25	0.31	2.50	−	−	−	−	0.03	−	−	−	−	−	−	−	−	−	13	残	144

表2 本発明合金及び比較例の特性評価結果 Table 2

	No.	引張強さ tensile strength (N/mm²)	導電率 (% IACS)	軟化温度 (℃)	破断の有無	ピンホール発生個数 (個/1000m)
本実施例	1	570	77	400	○	1
	2	610	75	420	○	3
	3	680	72	450	○	2
	4	600	79	410	○	6
	5	590	76	390	○	4
	6	640	83	410	○	5
	7	640	81	430	○	5
	8	680	69	460	○	6
	9	700	71	450	○	5
	10	710	76	440	○	4
比較例	11	500	86	310	○	4
	12	600	79	420	×	14
	13	660	56	450	○	7
	14	690	59	440	×	18
	15	700	58	460	×	21

[0029] A characterization result is shown in Table 2. As shown in Table 2, this invention alloy foil has the outstanding intensity, conductivity, thermal resistance, and productivity. On the other hand, since the example 11 of comparison does not contain Zr, it is an example in which intensity and thermal resistance are inferior. Moreover, as for Zn and the example 14 of comparison, since the total quantity of an accessory constituent exceeded the specification range, the conductivity of the example 13 of comparison is the lowered example. Moreover, the examples 12, 14, and 15 of comparison are examples which fracture generated in the manufacturing process since there was many inclusion, and the number of a pinhole increased.

[0030]

[Effect of the Invention] As explained above, according to this invention, the copper alloy foil which was excellent in intensity and thermal resistance compared with conventional rolling copper foil, and was excellent also in productivity again is obtained, and it is suitable for extensive uses, such as the reliable flexible circuit board and a base material for IC tape careers.

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[0004] On the other hand, if even the lamination foil of the above [the thickness of a foil] becomes thin in a manufacturing process, it will become difficult to roll out with the sufficient yield. Since especially the internal defect of inclusion etc. becomes the cause which fracture and a pinhole produce at the time of rolling, it reduces productivity, as a result causes increase of a manufacturing cost. Therefore, a material is expected for there to be little inclusion.

[0005] By the way, a deposited type copper alloy is used on the use of which the high intensity and high conductivity like the copper alloy for electronic equipment are required in many cases in recent years. A Cu-Cr-Zr system alloy is a typical deposited type copper alloy having high intensity and high conductivity, and the utilization as a charge of electronic equipment material is tried. According to the research result in this alloy, when detailed Cr and a detailed Cu3 Zr deposit particle arise in a copper matrix in aging deposit process, it is supposed that intensity and conductivity will rise and it is supposed that it is the size of the deposit particle which contributes to an on-the-strength rise 0.5 micrometers or less.

[0006] For example, the patent official report of a patent number No. (registration day : March 13, Heisei 8) 2501275 chooses zirconium 0.005 - 1wt% either or both sides chromium 0.01 - 2wt%, and becomes 60 ppm or less of oxygen, and a remainder real target from copper, and the size of a sludge is 50 micrometers or less. And a 0.5-50-micrometer sludge is 2 100-100000 pieces/mm. The copper alloy which had the conductivity and intensity which are characterized by existing is indicated. It has also indicated adding nickel, Sn, Fe, Co and Zn of the amount of specification, and the alloying element of Ti and other a large number into this alloy. however, the size which amounts to no less than 50 micrometers -- a **** thing sludge -- 100-100000 piece/mm2 existing -- if -- it is inapplicable as a rolling foil

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[Translation done.]

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EFFECT OF THE INVENTION

[Effect of the Invention] As explained above, according to this invention, the copper alloy foil which was excellent in intensity and thermal resistance compared with conventional rolling copper foil, and was excellent also in productivity again is obtained, and it is suitable for extensive uses, such as the reliable flexible circuit board and a base material for IC tape careers.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] Although it is realizable since the property in which intensity and conductivity rise when detailed Cr and a detailed Cu3 Zr deposit particle arise in a copper matrix in a Cu-Cr-Zr system alloy has the property in which Cr and Zr of an alloying element cannot dissolve easily with the copper of a matrix The big and rough crystallization object or big and rough sludge which does not contribute to improvement in one side and intensity tends to remain in a matrix. moreover, since the activity of these alloying elements is high Since it is easy to generate an oxide, a sulfide, a silicide, etc., the result of being easy to become the organization which these comparatively big particles distributed in the matrix is to be induced. In fact, for the above-mentioned patent number No. 2501275, a 0.5-50-micrometer sludge is 2 100-100000 pieces/mm. It reached and has indicated existing.

[0008] A Cu-Cr-Zr system alloy is an outstanding copper alloy which has high intensity and high conductivity fundamentally, and using this also for rolling copper foil is expected. However, if these big and rough particles exist, since it will become the cause which fracture and a pinhole produce at the time of rolling in putting a Cu-Cr-Zr system alloy in practical use as a copper alloy foil material, productivity is reduced, as a result increase of a manufacturing cost is caused.

[0009] Therefore, while having the intensity, the outstanding conductivity, and outstanding thermal resistance which can be used suitable for a flexible printed circuit board or IC tape careers, development of the Cu-Cr-Zr system copper alloy foil excellent also in productivity is demanded. Moreover, in such a copper alloy foil, it is also required to prevent the soldered joint section producing exfoliation with working heat in the use in a flexible printed circuit board etc.

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MEANS

[Means for Solving the Problem] As a result of repeating research of a Cu-Cr-Zr system alloy, while this invention persons adjust an alloy content by adding Zn to Cr and Zr By controlling and selecting manufacture conditions strictly and controlling a distribution of inclusion, such as a sludge in a matrix, a crystallization object, an oxide, a sulfide, and a silicide It is possible to make intensity, conductivity, thermal resistance, and productivity balance on high level. The bird clapper turned out that the further improvement of a strength property was possible by adding one or more sorts of Fe, Ti, and nickel, Sn, In, Mn, P, Mg, aluminum, B, As, Cd, Co, Te, Ag and Hf to this. Unlike the indication of the aforementioned patent number No. 2501275, the number of the inclusion of the size which the size of inclusion is 10 micrometers or less, and is 0.5-10 micrometers is 2 100 pieces/mm. It could consider as the following and the copper alloy rolling foil which can begin by this and can be used suitable for a flexible printed circuit board, IC tape career, etc. was obtained.
[0011] It is based on such knowledge. this invention Cr:0.02-0.4%, Zr:0.01-0.25%, Zn:0.02-2.0% is contained. as occasion demands Fe:0.05-1.8%, Ti:0.05-0.8% -- further -- the need -- nickel, Sn, In, and Mn -- One or more sorts of P, Mg, aluminum, B, As, Cd, Co, Te, Ag, and Hf : No less than 0.005 - 1.5 % of the weight is contained in a total amount. The remainder consists of copper and an unescapable impurity, and the size of inclusion is 10 micrometers or less. and the number of inclusion with a size of 0.5-10 micrometers -- 100 piece/mm2 It is characterized by being the following, and intensity and thermal resistance are markedly boiled rather than conventional copper foil, it improves, and a copper alloy foil also with still better productivity is offered.
[0012] In this invention with a term "inclusion" The cooling process after the solidification process at the time of casting (i.e., the solidification back), The sludge produced at a deposit reaction in the matrix of solid phase at the time of the cooling process after hot rolling, and aging annealing etc. (particle), The oxide which is an impurity which produces according to the segregation of the solidification process at the time of casting, and is generally produced by the reaction within a big and rough crystallization object (particle) and the molten metal at the time of the dissolution, a sulfide, a silicide, etc. are used as what includes the particle observed by microscope observation of this copper alloy in a matrix. "The size of inclusion" says the minimum diameter of circle which wraps the inclusion for inclusion in the bottom of microscope observation. "The number of inclusion" is the average number of the inclusion per [which were actually counted in the part under microscope observation] unit square mm. That is, after carrying out mirror polishing of the front face of a sample, in EPMA, it is 5000 times the scale factor of this, and the number of inclusion with a size [per unit square mm] of 0.5-50 micrometers is measured.
[0013]
[Embodiments of the Invention] The reason which limited alloy composition and the inclusion size as mentioned above in this invention is explained.
(Cr) Although Cr carries out the operation which deposits in a host phase and raises intensity by carrying out aging of the alloy after solution treatment, at less than 0.02 % of the weight, the effect of a request according [the content] to this operation is not acquired, but if it is made to contain exceeding 0.4%, on the other hand, big and rough Cr will remain in a host phase. Consequently, the fall of productivity will be caused by the fracture at the time of rolling, pinhole generating, etc. By such reason, Cr content determined it as 0.02 - 0.4% of the weight of the range.
[0014] (Zr) Although Zr had the operation which forms Cu and a compound by the aging treatment, deposits in a host phase, and strengthens this, the effect of a request according [the content] to the aforementioned

operation was not acquired, but since big and rough un-dissolving [Zr] came to contain and the fall of productivity caused after solution treatment when Zr was made to contain exceeding 0.25 % of the weight, on the other hand at less than 0.01 % of the weight, a Zr content determined it as 0.01 - 0.25 %.
[0015] (Zn) Although Zn was a component added in order for the soldered joint section to prevent producing exfoliation with working heat, at less than 0.02%, the effect of a request according [the content] to the aforementioned operation was not acquired, but when Zn was made to contain exceeding 2.0, on the other hand, the decline in conductivity determined Zn content as 0.02 - 2.0% from the bird clapper remarkably.
[0016] (Ti and Fe) Although Ti and Fe are added if needed in order to demonstrate the operation which forms the intermetallic compound of Ti and Fe into a host phase, and raises alloy intensity further as the result when the aging treatment of the alloy is carried out, at less than 0.05%, the intensity of a request according [these contents] to the above-mentioned operation is not obtained, respectively. On the other hand, when Ti content exceeds 0.8% or Fe content exceeds 1.8%, the big and rough inclusion which makes Ti and Fe a principal component comes to be contained, and productivity is checked remarkably.
[0017] (nickel, Sn, In, Mn, P, Mg, aluminum, B, As, Cd, Co, Te, Ag, Hf) Although each of these has the operation which raises intensity mainly by solid solution strengthening, without reducing the conductivity of an alloy, therefore one sort or two sorts or more of addition is made as occasion demands The effect of a request according that the content is less than 0.005% in a total amount to the aforementioned operation is not acquired, but when exceeding 1.5% in a total amount by one side, conductivity is degraded remarkably, and productivity also falls. For this reason, the content of nickel, Sn, In, Mn, P, Mg, aluminum, B, As, Cd, Co, Te, Ag, and Hf by which independent addition or two or more sorts of compound addition are made determined it as 0.005 - 1.5% in the total amount.
[0018] (Inclusion) By this alloy system, the particle of inclusion may exist in a matrix. Although the inclusion for obtaining intensity required for this alloy is small, the big and rough inclusion exceeding 0.5 micrometers is set like about [not contributing to an on-the-strength rise] and a roll turner, generates fracture and a pinhole, and causes a productivity fall. In order not to cause such fault, the upper limit of the size of this big and rough inclusion is set to 10 micrometers, and they are 2 / mm2 100 pieces/mm about the number of inclusion with a size of 0.5-10 micrometers. What is necessary is just to consider as the following.
[0019] Next, the manufacture method for obtaining this alloy is explained.
(The dissolution and casting) It is important to prevent generation of inclusion, such as a big and rough oxide, a sulfide, and a silicide, at a dissolution process. First, as the quality of the material of a crucible, carbon is desirable, and the use is not appropriate, in order for a molten metal to eat these away, and to involve in into a molten metal, or for internal insulation to be returned by Zr and to generate Zr oxide, when using the thing containing oxides, such as a magnesia, an alumina, and a silica. Moreover, if the dissolution raw material to be used has adhesion of an oil content, since a sulfide may be formed in a molten metal, it is not desirable. Therefore, when using return material, it should degrease or use of return material should be avoided. After the melt down of a dissolution raw material needs to reduce an oxygen density by covering a molten-metal front face with reducing gas, such as CO, or considering as vacuum atmosphere. It is desirable to set an oxygen density to 20 ppm or less by this.
[0020] (Homogenization heat treatment) Next, homogenization heat treatment conditions are described. In an ingot, the crystallization object formed when alloying elements including Cr and Zr segregated at the time of casting exists. In order to make these small in the process to a product, it is necessary to make a crystallization object small in this stage by carrying out enough, before hot-rolling homogenization heat treatment. It is necessary to specifically make preferably 800 degrees C or more of temperature in a hot rolling start time into 850 degrees C or more.
[0021] (Hot rolling) Next, hot rolling conditions are described. If temperature falls during rolling, when a deposit reaction progresses, big and rough-ization of a particle will take place. In such a case, a large particle will remain also in a product stage. Therefore, it is required during hot rolling for the temperature of material not to fall, and it is desirable for 700 degrees C or more to be 750 degrees C or more preferably about end temperature. In the cooling process after hot rolling, when a deposit reaction progresses, big and rough-ization of a particle takes place, so that a cooling rate is made late. In such a case, a large particle will remain also in a product stage. Therefore, it is required during hot rolling for the temperature of material not to fall, and it is

desirable for 700 degrees C or more to be 750 degrees C or more preferably about end temperature.
[0022] (Solution treatment) Liquid-ized processing is performed for obtaining the material of high intensity by the next aging treatment. The intensity after the increase of the amount of dissolution into the matrix of Cr and Zr and aging becomes [the one where processing temperature is higher] high. It is so good that processing temperature is high in order to acquire such an effect, and it is desirable to consider as 700 degrees C or more. Moreover, as for a cooling rate, it is desirable in the case of solution treatment for high intensity to be easy to be obtained and for the quicker one to specifically perform water cooling.
[0023] (Cold rolling) If it cold-rolls after solution treatment, a deposit at an aging process will be promoted and high intensity will be obtained. Moreover, in order to acquire this effect, it is desirable to make workability of cold rolling into 40% or more.
[0024] (Aging treatment) The aging treatment is required in order to raise intensity and conductivity, and it is performed at 300-700 degrees C. The reason for making aging-treatment temperature into 300-700 degrees C requires time for an aging treatment at less than 300 degrees C, and is for Cr and Zr to dissolve, if it is not economical and exceeds 700 degrees C, and for the intensity and the conductive improvement by the age-hardening not to arise. Then, the last cold rolling and stress relief tempering are performed.

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EXAMPLE

[Example] this invention is explained based on an example and the example of comparison. First, electrolytic copper or an oxygen free copper is used as the main raw material, and it is a copper chromium hardener. A copper zirconium hardener, zinc, titanium, nickel, tin, an indium, manganese, magnesium mild steel, silicon, a copper Lynn hardener, aluminum, boron, an arsenic, cadmium, cobalt, a tellurium, and silver were made into the auxiliary material, and the copper alloy of the various component composition shown in Table 1 with a RF fusion furnace was [inside of vacuum, or Ar atmosphere] under dissolution using the crucible made from carbon, and it ingoted, and cast to the ingot with a thickness of 30mm. Next, according to the process mentioned above, the foil with a thickness of 0.035mm was created from each of these ingots, and it evaluated about "intensity", "conductivity", and "thermal resistance." About "intensity", tensile strength was measured in the tension tester. Conductivity showed "conductivity." "Thermal resistance" asked for the temperature which tensile strength reduces by half from before heating in heating for 1 hour as a softening temperature. In addition, about "the number of inclusion", after carrying out mirror polishing of the front face of a sample, in EPMA, it is 5000 times the scale factor of this, and the number of inclusion with a size [per unit square mm] of 0.5-50 micrometers was measured.
[0026] Moreover, thickness:0.035mm, width-of-face:450mm, length: The 5000m foil was created and evaluation of "productivity" was also performed. The inner fracture generating situation and the pinhole generating situation in a product stage estimated "productivity" like the roll turner. About "fracture", the case where fracture did not occur was made as O, and the case where it generated was made into x. About the "pinhole", it carried out by measuring the generating number of a pinhole with a diameter [per 1000m] of 0.5mm or more.
[0027]
[Table 1]

[0028]
[Table 2]

表１　本発明合金および比較例

	No.	化学成分 (wt%)																				介在物数 (個/mm²)
		Cr	Zr	Zn	Ti	Fe	Sn	Ni	Si	Mg	P	In	Mn	Al	B	As	Cd	Co	Te	Ag	O (ppm)	Cu及び不純物	
本実施例	1	0.18	0.15	0.19	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	6	残	61
	2	0.26	0.08	0.28	–	–	0.07	–	–	–	–	–	–	–	–	–	–	–	–	–	10	残	65
	3	0.24	0.14	0.42	–	–	–	0.04	–	–	0.03	–	–	–	–	–	–	0.04	–	–	9	残	68
	4	0.22	0.18	0.26	–	–	–	–	0.15	–	–	–	0.09	–	–	–	–	–	–	–	13	残	88
	5	0.27	0.09	0.60	–	–	–	–	–	0.28	–	–	–	–	–	0.02	–	–	–	0.02	12	残	76
	6	0.34	0.12	0.19	–	–	–	–	–	–	–	0.06	–	–	–	–	–	–	0.04	–	8	残	78
	7	0.36	0.16	0.29	–	–	–	–	–	–	–	–	–	0.04	–	–	0.07	–	–	–	14	残	84
	8	0.20	0.18	0.72	0.22	0.29	–	–	–	–	–	–	–	–	–	–	–	–	–	–	13	残	88
	9	0.22	0.09	0.38	0.23	0.44	–	–	0.26	–	0.02	–	–	–	–	–	–	–	–	–	10	残	79
	10	0.23	0.14	0.89	0.37	0.61	0.11	–	–	0.18	–	–	0.07	–	0.09	–	–	–	–	–	8	残	85
比較例	11	0.03	–	0.21	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	7	残	80
	12	0.67	0.11	0.31	–	–	–	–	0.09	–	–	–	–	–	–	–	–	–	–	–	14	残	120
	13	0.26	0.14	2.12	0.31	0.62	–	1.02	0.21	–	–	–	–	–	–	0.02	–	–	–	–	8	残	89
	14	0.31	0.08	0.25	0.22	0.41	1.10	0.69	–	–	0.03	–	–	–	–	–	–	–	–	–	9	残	133
	15	0.29	0.22	0.25	0.31	2.50	–	–	–	–	0.03	–	–	–	–	–	–	–	–	–	13	残	144

表2 本発明合金及び比較例の特性評価結果

	No.	引張強さ (N/mm²)	導電率 (% IACS)	軟化温度 (℃)	破断の有無	ピンホール発生個数 (個/1000m)
本実施例	1	570	77	400	○	1
	2	610	75	420	○	3
	3	680	72	450	○	2
	4	600	79	410	○	6
	5	590	76	390	○	4
	6	640	83	410	○	5
	7	640	81	430	○	5
	8	680	69	460	○	6
	9	700	71	450	○	5
	10	710	76	440	○	4
比較例	11	500	86	310	○	4
	12	600	79	420	×	14
	13	660	56	450	○	7
	14	690	59	440	×	18
	15	700	58	460	×	21

[0029] A characterization result is shown in Table 2. As shown in Table 2, this invention alloy foil has the outstanding intensity, conductivity, thermal resistance, and productivity. On the other hand, since the example 11 of comparison does not contain Zr, it is an example in which intensity and thermal resistance are inferior. Moreover, as for Zn and the example 14 of comparison, since the total quantity of an accessory constituent exceeded the specification range, the conductivity of the example 13 of comparison is the lowered example. Moreover, the examples 12, 14, and 15 of comparison are examples which fracture generated in the manufacturing process since there was many inclusion, and the number of a pinhole increased.

[Translation done.]